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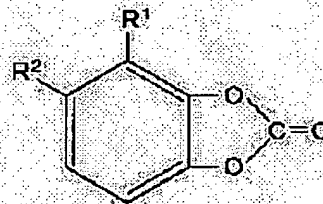
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(54) SECONDARY POWER SOURCE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a secondary power source capable of rapid charging and discharging and having high withstand voltage, high capacity, high energy density and high charge and discharge cycle reliability by having a positive electrode including the activated carbon, a negative electrode including a carbon material for storing and releasing the lithium ion, and the organic electrolyte containing the lithium salt and a specified compound.

SOLUTION: A compound expressed by the formula is used in this secondary power source. (In the formula, R₁, R₂ are each carbon atom or straight chain or branch alkyl group having 1-10 carbons). Desirably, concentration of the compound expressed with the formula is set at 0.1-15 wt.%, and the solvent of the organic electrolyte contains propylene carbonate at 70 wt.% or more, and as the carbon material, a graphite carbon material having 0.335-0.338 nm of spacing of a [002] plane is used, and the lithium ion is previously stored in the carbon material by a chemical method or an electrochemical method. Thickness of a negative electrode is set at 7-70% of a positive electrode.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] The withstand voltage of this invention is high and it is related with the secondary power supply which is excellent in charge-and-discharge cycle reliability.

[0002]

[Description of the Prior Art] The polarizable electrode to which a positive electrode and a negative electrode make activated carbon a subject is used for the electrode of the conventional electric double layer capacitor. The withstand voltages of an electric double layer capacitor are 2.5-3.3V, when 1.2V and the organic system electrolytic solution will be used, if the drainage system electrolytic solution is used. Since the energy of an electric double layer capacitor is proportional to the square of a withstand voltage, the direction of the organic high electrolytic solution of a withstand voltage is a high energy from the drainage system electrolytic solution. However, also with the electric double layer capacitor which used the organic electrolytic solution, the energy density is 1/10 or less [of rechargeable batteries such as a lead accumulator,], and improvement in the further energy density is needed.

[0003] On the other hand, the secondary power supply of upper limit voltage 3V which use as a negative electrode the electrode which the electrode which makes activated carbon a subject was made [electrode] into the positive electrode, and carried out occlusion of the lithium ion to the carbon material whose spacing of the [002] sides by the X diffraction is 0.338-0.356nm beforehand is proposed by JP,64-14882,A. The cell which uses for a negative electrode the carbon material which carried out occlusion of the lithium ion for the lithium ion to occlusion and the carbon material from which it may be desorbed by the chemical method or electrochemical process beforehand is proposed by JP,8-107048,A. The secondary power supply of upper limit voltage 4V which has the negative electrode which the porosity charge collector [occlusion] which does not form a lithium ion and does not form a lithium and an alloy for the carbon material from which it may be desorbed is made to support is proposed by JP,9-55342,A.

[0004] The secondary power supply which used activated carbon for the positive electrode and used for the negative electrode occlusion and the carbon material from which it may be desorbed for the lithium ion can make the conventional positive electrode and a negative electrode the high voltage and high capacity from the electric double layer capacitor which used activated carbon. If the **** graphite system carbon material of lithium ion occlusion desorption potential is especially used for a negative electrode in this secondary power supply, it will be made more to high capacity. However, if a graphite system carbon material is not the electrolytic solution which uses ethylene carbonate as the main solvent, this electrolytic solution has the problem that hot stability is inadequate, to the ability not to **** [occlusion and] to the positive electrode which used activated carbon in a lithium ion.

[0005] Moreover, there is a rechargeable lithium-ion battery in the secondary power supply in which high current charge and discharge are possible in addition to an electric double layer capacitor and the above-mentioned secondary power supply.

Although the rechargeable lithium-ion battery had the property of the high voltage and high capacity compared with the electric double layer capacitor, resistance was high and the remarkable short problem had a life by the rapid charge-and-discharge cycle compared with the electric double layer capacitor.

[0006]

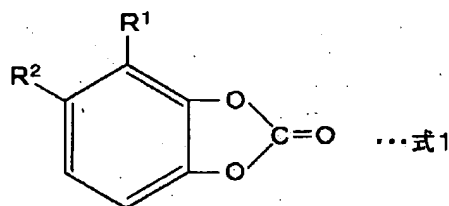
[Problem(s) to be Solved by the Invention] Then, rapid charge and discharge are possible, an energy density is high at a high withstand voltage and high capacity, and this invention aims at offering a secondary power supply with high charge-and-discharge cycle reliability.

[0007]

[Means for Solving the Problem] this invention offers the secondary power supply which has the organic electrolytic solution containing the compound (however, R1 and R2 express the alkyl group of a carbon atom or the shape of a straight chain of carbon numbers 1-10, and the letter of branching independently in a formula 1, respectively.) expressed in lithium salt and a formula 1 as the negative electrode containing occlusion and the carbon material from which it may be desorbed in the positive electrode containing activated carbon, and a lithium ion.

[0008]

[Formula 2]



[0009] In this specification, the thing which joined the negative electrode and charge collector which make a lithium ion occlusion and make a subject the carbon material from which it may be desorbed, and was made to unify is called negative-electrode object. It considers as the definition with the same said of a positive-electrode object. Moreover, although a rechargeable battery and electric double layer capacitor is also one sort of a secondary power supply, on these specifications, the secondary power supply of the specific composition which contains in a negative electrode occlusion and the carbon material from which it may be desorbed for a lithium ion in a positive electrode including activated carbon is only called secondary power supply.

[0010] As a solvent of the electrolytic solution in this invention, ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, sulfolane, 1, and 2-dimethoxyethane etc. is mentioned, it is independent or these can be used as two or more sorts of mixed solvents. It is desirable that it is the solvent with which the activated carbon of a positive electrode contains propylene carbonate at a stable point to voltage impression especially, and it is desirable that it is the solvent with which especially propylene carbonate is contained 70% of the weight or more.

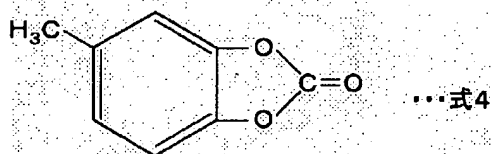
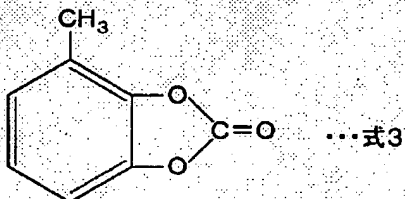
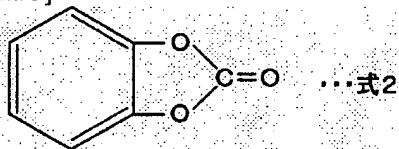
[0011] Although a graphite system carbon material, low-temperature baked-carbon material, a hard carbon, etc. are mentioned considering the lithium ion of the negative electrode in this invention as occlusion and a carbon material from which it may be desorbed, lithium ion occlusion and a graphite system carbon material especially **** in the potential of desorption are desirable. However, in the solution which dissolved lithium salt in the solvent containing propylene carbonate, whether it is going to carry out occlusion of the lithium ion to graphite system material by electrochemical process, or is going to charge the aforementioned solution as the electrolytic solution and is going to carry out occlusion of the lithium ion, electrolysis of propylene carbonate takes place in the neighborhood whose potential to a lithium reference pole is about 0.8V, and the occlusion of the lithium ion cannot be carried out.

[0012] However, if the compound (it is hereafter written as a compound 1) expressed with a formula 1 by the solution which dissolved lithium salt in the solvent containing propylene carbonate is added, decomposition of propylene carbonate will be suppressed and the occlusion of the lithium ion can be carried out also to a graphite system carbon material.

[0013] It sets to a compound 1 and is R1. And R2 It is the alkyl group of a hydrogen atom or the shape of a straight chain of carbon numbers 1-10, and the letter of branching independently, respectively. R1 And R2 If a carbon number increases, it will be hard coming to dissolve in the electrolytic solution. As a compound 1, the catechol carbonate specifically expressed with a formula 2, 3-methylcatechol carbonate expressed with a formula 3, 4-methylcatechol carbonate expressed with a formula 4 are desirable.

[0014]

[Formula 3]



[0015] Although the detail of the mechanism of decomposition suppression of the propylene carbonate by adding a compound 1 is not clear, the compound 1 in a propylene carbonate solution works as a scavenger of the intermediate-field radical generated from the propylene carbonate molecule in the electrolysis process of the propylene carbonate at the time of the lithium ion occlusion of graphite system material, and it is thought that the surface coat which has lithium ion conductivity is formed in a graphite system material-list side. Consequently, it is thought that decomposition of the further propylene carbonate is prevented.

[0016] As for the concentration in the electrolytic solution of a compound 1, it is desirable that it is 0.1 - 15 % of the weight. At less than 0.1 % of the weight, the effect which adds this compound is small and cannot carry out occlusion of the lithium ion to graphite system material in the propylene carbonate solution containing a lithium ion. If it exceeds 15 % of the weight, the capacity of a secondary power supply will become small and the fall of the capacity by the charge-and-discharge cycle will become large. It is especially desirable that it is 0.5 - 5 % of the weight.

[0017] It is the electrode to which the electrode and negative electrode to which a rechargeable lithium-ion battery makes a lithium content transition-metals oxide a subject in a positive electrode make a lithium ion occlusion, and make a subject the carbon material from which it may be desorbed, and a lithium ion is desorbed from the lithium content transition-metals oxide of a positive electrode by charge, occlusion of the lithium ion of a negative electrode is carried out to occlusion and the carbon material from which it may be desorbed, a lithium ion is desorbed from a negative electrode by electric discharge, and occlusion of the lithium ion is carried out to a Therefore, the lithium ion in the electrolytic solution essentially does not participate in the charge and discharge of a cell.

[0018] On the other hand, the anion in the electrolytic solution sticks to the secondary power supply of this invention by charge at the activated carbon of a positive electrode, and occlusion of the lithium ion in the electrolytic solution is carried out in the lithium ion of a negative electrode to occlusion and the carbon material from which it may be desorbed. And a lithium ion is desorbed from a negative electrode by electric discharge, and an anion carries out desorption in a positive electrode. That is, with the secondary power supply of this invention, the solute of the electrolytic solution is essentially participating in charge and discharge, and the mechanism of charge and discharge differs from the lithium ion battery. And since occlusion and ****ing do not have a lithium ion in the positive active material itself and there is no degradation of the positive electrode accompanying the occlusion of a lithium ion and desorption like a rechargeable lithium-ion battery, the secondary power supply of this invention has little degradation by the charge-and-discharge cycle, and it is excellent in long-term reliability.

[0019] It is desirable to carry out occlusion of the lithium ion to the carbon material of a negative electrode by the chemical method or electrochemical process beforehand in this invention. It is immersed into the organic solvent which dissolved the electrolytic solution or the other lithium salt as the chemical method where a negative-electrode carbon material and a lithium metal are contacted, for example, and there is the method of making ionize a lithium and carrying out occlusion to a negative-electrode carbon material. For example, a negative-electrode carbon material and a lithium metal are made to counter through separator as electrochemical process, and there is a method of charging the aforementioned negative-electrode carbon material by the constant current or the constant voltage in the electrolytic solution.

[0020] Moreover, if it forms so that positive-electrode capacity and negative-electrode capacity may become almost equivalent, even if it does not carry out occlusion of the lithium ion to the carbon material of a negative electrode by the chemical method or electrochemical process beforehand as mentioned above, potential of a negative electrode will fully be made to ** by charge of a secondary power supply. That is, by charge of a secondary power supply, since negative-electrode capacity is larger than positive-electrode capacity in the thickness of a positive electrode and a negative electrode being of the same grade, since the potential of a negative electrode does not fully become **, if occlusion of the lithium ion is not beforehand carried out to a negative electrode, it does not become the secondary power supply of the high voltage. However, if negative-electrode capacity is almost the same as positive-electrode capacity, potential of a negative electrode will fully be made to ** only in charge of a secondary power supply.

[0021] Specifically, it is desirable that the thickness of the negative electrode which counters through separator to the thickness of a positive electrode is 7 - 70% and further 15 - 40%. If the ratio of the thickness of a positive electrode and a negative electrode is this range, the capacity of a positive electrode and the capacity of a negative electrode can be balanced, and the secondary power supply of a high withstand voltage can be constituted. And as for especially the thickness of a positive electrode, it is desirable that it is 100-220 micrometers 80-250 micrometers. Capacity of a secondary power supply cannot be enlarged in less than 80 micrometers. Moreover, when exceeding 250 micrometers, since resistance goes up at the time of charge and discharge, for carrying out rapid charge and discharge, it is not practical.

[0022] Moreover, the thickness of a negative electrode specifically has desirable 10-150 micrometers in this case. Forming is difficult for a negative electrode with a thickness of less than 10 micrometers. The thickness of a positive electrode is [the thickness of 100-200 micrometers and a negative electrode] 20-50 micrometers especially preferably. In addition, although you may form in both sides in this invention even if it forms a positive electrode and a negative electrode in one side of a charge collector, the thickness of a positive electrode here and a negative electrode shall show the electrode layer thickness currently formed in one side of a charge collector, even when formed in both sides of a charge collector.

[0023] As for the activated carbon contained in a positive electrode, it is desirable that specific surface area is 800-3000m² / g. Although the raw material of activated carbon and activation conditions are not limited, for example as a raw material, coconuts are mentioned for phenol resin, petroleum coke, etc., and a steam activation method, a melting alkali aktivationsmethode, etc. are mentioned as the activation method. especially -- coconuts -- or the activated carbon obtained use / phenol resin / as a raw material] by carrying out steam activation is desirable In order to make resistance of a positive

electrode low, it is also desirable to include conductive carbon black or a conductive graphite as electric conduction material all over a positive electrode, and, as for electric conduction material, it is desirable at this time to be contained 0.1 to 20% of the weight all over a positive electrode.

[0024] After mixing and kneading a polytetrafluoroethylene, for example as a binder into the mixture of activated carbon powder and electric conduction material as the production method of a positive-electrode object, it fabricates in the shape of a sheet, and considers as a positive electrode, and there is the method of using an electroconductive glue at a charge collector and fixing this. Moreover, the varnish which dissolved the polyvinylidene fluoride, the polyamidoimide, the polyimide, etc. as a binder is made to distribute activated carbon powder and electric conduction material powder, by the doctor blade method etc., on a charge collector, coating of this liquid may be carried out, and it may be dried and obtained. As for the amount of the binder contained all over a positive electrode, it is desirable that it is 1 - 20 % of the weight from the balance of the intensity of a positive-electrode object and properties, such as capacity.

[0025] As for occlusion and the carbon material from which it may be desorbed, in this invention, it is desirable that the spacing of the [002] sides according a lithium ion to an X diffraction is 0.335-0.410nm. All can be used although there are material, a difficulty graphite nature carbon material, etc. into which the heat treatment temperature of a natural graphite, an artificial graphite, petroleum coke, a mesophase pitch system carbon material, or a vapor-growth carbon fiber was changed among 800-3000 degrees C at occlusion and the carbon material from which it may be desorbed about a lithium ion. Especially, the graphite system carbon material whose spacing of a low point to [002] sides especially resistance is 0.335-0.338nm is desirable.

[0026] As the above-mentioned graphite system carbon material, a mesophase pitch based carbon fiber, a meso carbon micro bead, the carbon material that heat-treated the vapor-growth carbon material above 2800 degrees C, a natural graphite, etc. are specifically mentioned.

[0027] A polytetrafluoroethylene can be kneaded as a binder like a positive electrode, it can fabricate in the shape of a sheet, a negative electrode can be formed, a charge collector can be made to be able to paste using an electroconductive glue, and the negative-electrode object in this invention can be acquired. Moreover, use a polyvinylidene fluoride, a polyamidoimide, or a polyimide as a binder, the solution made to dissolve the resin used as a binder or its precursor in an organic solvent is made to distribute the aforementioned carbon material, and there is also the method of carrying out coating to a charge collector, making it dry, and acquiring. Each of these methods is desirable.

[0028] In the method of carrying out coating of the aforementioned solution to a charge collector, and acquiring a negative-electrode object, although the solvent in which the resin used as a binder or its precursor is dissolved is not limited, the resin which constitutes a binder, or its precursor can be dissolved easily, and since acquisition is also easy, a N-methyl-2-pyrrolidone (henceforth NMP) is desirable. Here, the precursor of a polyvinylidene fluoride, the precursor of a polyamidoimide, or the precursor of a polyimide means what carries out a polymerization and serves as a polyvinylidene fluoride, a polyamidoimide, or a polyimide, respectively by heating.

[0029] The binder obtained as mentioned above is hardened by heating, and is excellent in chemical resistance, a mechanical property, and dimensional stability. As for the temperature of heat treatment, it is desirable that it is 200 degrees C or more. If it is 200 degrees C or more, even if it is the precursor of a polyamidoimide, or the precursor of a polyimide, a polymerization will usually be carried out, and it will become a polyamidoimide or a polyimide, respectively. Moreover, the atmosphere to heat-treat has the desirable bottom of inert atmospheres, such as nitrogen and an argon, or reduced pressure of 1 or less torr. In order for there to be resistance over the organic electrolytic solution used by this invention and to remove moisture from a negative electrode, even if a polyamidoimide or a polyimide carries out about 300-degree C heating at high temperature or heating under reduced pressure, it is tolerant enough.

[0030] In this invention, if the glue line which consists of a polyamidoimide or a polyimide is made to intervene between a negative electrode and a charge collector, the adhesive strength of a negative electrode and a charge collector will become firmer. In this case, coating of the varnish which made the solvent dissolve a polyamidoimide, polyimides, or these precursors in a charge collector beforehand is carried out by coating methods, such as a doctor blade method, it dries, a glue line is formed, and a negative electrode is formed on this. Moreover, if the varnish which forms a glue line is made to distribute electric conduction material, such as copper and a graphite, since the contact resistance of a negative electrode and a charge collector can be reduced, it is desirable. The varnish containing this electric conduction material can also be made to intervene as an electroconductive glue also between these layers and charge collectors at the time of fabricating the layer containing activated carbon in the shape of a sheet.

[0031] As for occlusion and the weight ratio of the carbon material and binder from which it may be desorbed, in this invention, 70:30-96:4 are desirable in the lithium ion in a negative electrode. If there are more binders than 30 % of the weight, negative-electrode capacity will become small. The effect as a binder becomes it weak that a binder is less than 4 % of the weight, and ablation with a negative electrode and a charge collector increases.

[0032] the lithium salt contained in the organic electrolytic solution in this invention -- LiPF₆, LiBF₄ and LiClO₄, LiN(SO₂CF₃)₂, CF₃SO₃Li, LiC(SO₂CF₃)₃, and LiAsF₆ And LiSbF₆ from -- one or more sorts chosen from the becoming group are desirable The concentration of the lithium salt in the electrolytic solution has 0.1 - 2.5 mol/L, and desirable further 0.5 - 2 mol/L.

[0033]

[Example] Next, this invention is not limited by these although an example (Examples 1-10) and the example of comparison (Examples 11-12) explain this invention still more concretely. In addition, the dew-point performed all of production and

measurement of the cell of Examples 1-12 in the argon glove box -60 degrees C or less.

[0034] [Example 1] After having added ethanol, kneading 80 % of the weight of activated carbon of specific surface area of 2000m² / g obtained by the steam activation method by using phenol resin as a raw material, 10 % of the weight of conductive carbon black, and the mixture that consists of 10 % of the weight of polytetrafluoroethylenes as a binder and rolling it out, the vacuum drying was carried out at 200 degrees C for 2 hours, and the electrode sheet with a thickness of 150 micrometers was obtained. The 4cmx6cm electrode was obtained from this electrode sheet, and it joined to the aluminum foil using the electroconductive glue which uses a polyamidoimide as a binder, heat-treated at 300 degrees C under reduced pressure for 10 hours, and considered as the positive-electrode object.

[0035] Next, the solution which dissolved in NMP was made to distribute a polyamidoimide using the graphite system carbon material whose spacing of [002] sides is 0.338nm considering a lithium ion as occlusion and a carbon material from which it may be desorbed, and it applied to the charge collector which consists of copper, and dried, and the negative electrode was formed on the charge collector. Occlusion, and the carbon material and polyamidoimide from which it may be desorbed were 9:1 in the weight ratio about the lithium ion in a negative electrode. This was further pressed with the roll-press machine, area of a negative electrode was set to 6cmx4cm, and thickness was set to 15 micrometers, and it heat-treated at 260 degrees C under reduced pressure for 10 hours, and considered as the negative-electrode object.

[0036] Each electrode side was made to counter through the separator made from polypropylene, the above-mentioned positive-electrode object and the above-mentioned negative-electrode object were pinched with the pinching board, and the element was produced. They are 2 % of the weight and LiBF₄ about catechol carbonate (formula 2) to propylene carbonate. The solution which dissolved by the concentration of 1 mol/L was made into the electrolytic solution, the aforementioned element was fully infiltrated, and initial capacity was measured in the ranges from 4.2V to 3V. Then, charge and discharge current 10 mA/cm². The charge-and-discharge cycle was performed in the ranges from 4.2V to 3V, the capacity after 2000 cycles was measured, and the rate of change of capacity was computed. A result is shown in Table 1.

[0037] [Example 2] Except having used 3-methylcatechol carbonate (formula 3) instead of catechol carbonate (formula 2), the secondary power supply was obtained like Example 1, and it was similarly estimated as Example 1. A result is shown in Table 1.

[0038] [Example 3] Except having used 4-methylcatechol carbonate (formula 4) instead of catechol carbonate (formula 2), the secondary power supply was obtained like Example 1, and it was similarly estimated as Example 1. A result is shown in Table 1.

[0039] [Example 4] Except having changed the amount of catechol carbonate (formula 2) to 0.05% of the weight, the secondary power supply was obtained like Example 1, and it was similarly estimated as Example 1. A result is shown in Table 1.

[0040] [Example 5] Except having changed the amount of catechol carbonate (formula 2) to 20% of the weight, the secondary power supply was obtained like Example 1, and it was similarly estimated as Example 1. A result is shown in Table 1.

[0041] [Example 6] The positive-electrode object with which electrode side 4cmx6cm and the positive electrode with a thickness of 150 micrometers were joined to the charge collector was acquired like Example 1 except having used the activated carbon of specific surface area of 2000m² / g obtained by the steam activation method by using coconuts as a raw material instead of phenol resin.

[0042] Next, the negative-electrode object with which electrode side 4cmx6cm and the negative electrode with a thickness of 200 micrometers were joined to the charge collector was acquired like Example 1 except having used the graphite system carbon material whose spacing of [002] sides is 0.337nm considering a lithium ion as occlusion and a carbon material from which it may be desorbed. This negative electrode is made into an operation pole, and by making into a counter electrode and a reference pole what fixed the lithium metal to a nickel mesh, occlusion of the lithium ion was carried out until it became a negative electrode with 290 mAh/g by electrochemical process in the same electrolytic solution as Example 1. Except having used the above-mentioned positive-electrode object and the above-mentioned negative-electrode object, the secondary power supply was obtained like Example 1, and it was similarly estimated as Example 1. A result is shown in Table 1.

[0043] [Example 7] Except having used 3-methylcatechol carbonate (formula 3) instead of catechol carbonate (formula 2), the secondary power supply was obtained like Example 6, and it was similarly estimated as Example 6. A result is shown in Table 1.

[0044] [Example 8] Except having used 4-methylcatechol carbonate (formula 4) instead of catechol carbonate (formula 2), the secondary power supply was obtained like Example 6, and it was similarly estimated as Example 6. A result is shown in Table 1.

[0045] [Example 9] Except having changed the amount of catechol carbonate (formula 2) to 0.05% of the weight, the secondary power supply was obtained like Example 6, and it was similarly estimated as Example 6. A result is shown in Table 1.

[0046] [Example 10] Except having changed the amount of catechol carbonate (formula 2) to 20% of the weight, the secondary power supply was obtained like Example 1, and it was similarly estimated as Example 6. A result is shown in Table 1.

[0047] [Example 11] LiBF₄ of 1 mol/L which does not add catechol carbonate (formula 2) as the electrolytic solution Except having used the included propylene carbonate solution, the secondary power supply was obtained like Example 1, and it was similarly estimated as Example 1. A result is shown in Table 1.

[0048] [Example 12] LiBF₄ of 1 mol/L which does not add catechol carbonate (formula 2) as the electrolytic solution Except

having used the included propylene carbonate solution, the secondary power supply was obtained like Example 6, and it was similarly estimated as Example 1. A result is shown in Table 1.

[0049]

[Table 1]

	初期容量 (mA h)	容量変化率 (%)
例 1	1. 9 5	- 6. 8
例 2	1. 9 2	- 7. 3
例 3	1. 9 4	- 6. 9
例 4	1. 6 7	- 1 1. 7
例 5	1. 6 2	- 1 2. 9
例 6	2. 4 3	- 5. 4
例 7	2. 4 1	- 5. 7
例 8	2. 3 1	- 5. 8
例 9	2. 3 0	- 9. 6
例 1 0	2. 2 8	- 1 0. 4
例 1 1	0. 1 9	- 7 1. 6
例 1 2	0. 2 1	- 6 8. 9

[0050]

[Effect of the Invention] According to this invention, since the stable electrolytic solution can be used also to a negative electrode also to a positive electrode in a charge-and-discharge cycle, a withstand voltage is high and capacity can offer a large secondary power supply with high rapid charge-and-discharge cycle reliability.

[Translation done.]

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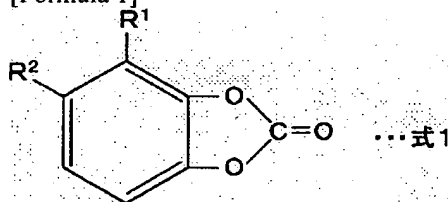
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CLAIMS

[Claim(s)]

[Claim 1] The secondary power supply characterized by having the organic electrolytic solution containing the compound (however, R1 and R2 expressing the alkyl group of a carbon atom or the shape of a straight chain of carbon numbers 1-10, and the letter of branching independently in a formula 1, respectively.) expressed in lithium salt and a formula 1 as the negative electrode containing occlusion and the carbon material from which it may be desorbed in the positive electrode containing activated carbon, and a lithium ion.

[Formula 1]



[Claim 2] The secondary power supply according to claim 1 whose concentration of the compound expressed with the formula 1 in the electrolytic solution is 0.1 - 15 % of the weight.

[Claim 3] The solvent of the organic electrolytic solution is a secondary power supply according to claim 1 or 2 which contains propylene carbonate 70% of the weight or more.

[Claim 4] The aforementioned carbon material is a secondary power supply according to claim 1, 2, or 3 which is the graphite system carbon material whose spacing of [002] sides is 0.335-0.338nm.

[Claim 5] The aforementioned carbon material is a secondary power supply according to claim 1, 2, 3, or 4 to which occlusion of the lithium ion is beforehand carried out by the chemical method or electrochemical process.

[Claim 6] A negative electrode is a secondary power supply according to claim 1, 2, 3, or 4 whose thickness is 7 - 70% of the thickness of a positive electrode.

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(54) 【発明の名称】 二次電源

(57) 【要約】

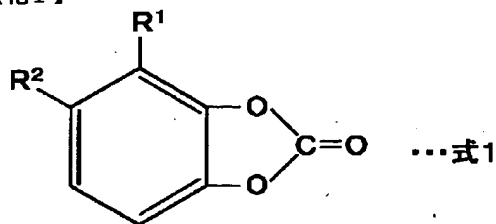
【課題】耐電圧が高く、容量が大きく、かつ充放電サイクル信頼性に優れた二次電源の提供。

【解決手段】活性炭を含む正極と、リチウムイオンを吸蔵、脱離しうる炭素材料を含む負極と、リチウム塩とカテコールカーボネート類とを含む有機電解液と、を有することを特徴とする二次電源。

【特許請求の範囲】

【請求項1】活性炭を含む正極と、リチウムイオンを吸蔵、脱離しうる炭素材料を含む負極と、リチウム塩と式1で表される化合物（ただし、式1において R^1 、 R^2 はそれぞれ独立に炭素原子又は炭素数1～10の直鎖状又は分岐状のアルキル基を表す。）を含む有機電解液と、を有することを特徴とする二次電源。

【化1】



【請求項2】電解液中の式1で表される化合物の濃度が0.1～15重量%である請求項1に記載の二次電源。

【請求項3】有機電解液の溶媒は、プロピレンカーボネートを70重量%以上含む請求項1又は2に記載の二次電源。

【請求項4】前記炭素材料は、[002]面の面間隔が0.335～0.338nmの黒鉛系炭素材料である請求項1、2又は3に記載の二次電源。

【請求項5】前記炭素材料は、あらかじめ化学的方法又は電気化学的方法によりリチウムイオンが吸蔵されている請求項1、2、3又は4に記載の二次電源。

【請求項6】負極は、厚さが正極の厚さの7～70%である請求項1、2、3又は4に記載の二次電源。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、耐電圧が高く、充放電サイクル信頼性に優れた二次電源に関する。

【0002】

【従来の技術】従来の電気二重層キャパシタの電極には、正極、負極ともに活性炭を主体とする分極性電極が使用されている。電気二重層キャパシタの耐電圧は、水系電解液を使用すると1.2V、有機系電解液を使用すると2.5～3.3Vである。電気二重層キャパシタのエネルギーは耐電圧の2乗に比例するので、耐電圧の高い有機電解液の方が水系電解液より高エネルギーである。しかし、有機電解液を使用した電気二重層キャパシタでもそのエネルギー密度は鉛蓄電池等の二次電池の1/10以下であり、さらなるエネルギー密度の向上が必要とされている。

【0003】これに対し、特開昭64-14882には、活性炭を主体とする電極を正極とし、X線回折による[002]面の面間隔が0.338～0.356nmである炭素材料にあらかじめリチウムイオンを吸蔵させた電極を負極とする上限電圧3Vの二次電源が提案されている。特開平8-107048には、リチウムイオン

を吸蔵、脱離しうる炭素材料にあらかじめ化学的方法又は電気化学的方法でリチウムイオンを吸蔵させた炭素材料を負極に用いる電池が提案されている。特開平9-55342には、リチウムイオンを吸蔵、脱離しうる炭素材料をリチウムと合金を形成しない多孔質集電体に担持させる負極を有する、上限電圧4Vの二次電源が提案されている。

【0004】正極に活性炭を用い、負極にリチウムイオンを吸蔵、脱離しうる炭素材料を用いた二次電源は、従来の正極、負極ともに活性炭を用いた電気二重層キャパシタより高電圧かつ高容量とすることができる。特に、この二次電源において負極にリチウムイオン吸蔵脱離電位の卑な黒鉛系炭素材料を用いると、より高容量にできる。ところが、黒鉛系炭素材料はエチレンカーボネートを主溶媒とする電解液でなければリチウムイオンを吸蔵、脱離できないのに対し、この電解液は活性炭を用いた正極に対しては高温における安定性が不充分である問題がある。

【0005】また、電気二重層キャパシタ、上記二次電源以外に、大電流充放電可能な二次電源にはリチウムイオン二次電池がある。リチウムイオン二次電池は電気二重層キャパシタに比べて高電圧かつ高容量という性質を有するが、抵抗が高く、急速充放電サイクルによる寿命が電気二重層キャパシタに比べ著しく短い問題があった。

【0006】

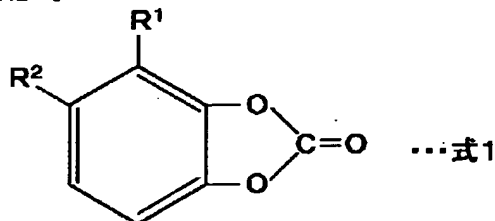
【発明が解決しようとする課題】そこで本発明は、急速充放電が可能で高耐電圧かつ高容量でエネルギー密度が高く、充放電サイクル信頼性の高い二次電源を提供することを目的とする。

【0007】

【課題を解決するための手段】本発明は、活性炭を含む正極と、リチウムイオンを吸蔵、脱離しうる炭素材料を含む負極と、リチウム塩と式1で表される化合物（ただし、式1において R^1 、 R^2 はそれぞれ独立に炭素原子又は炭素数1～10の直鎖状又は分岐状のアルキル基を表す。）を含む有機電解液と、を有する二次電源を提供する。

【0008】

【化2】



【0009】本明細書において、リチウムイオンを吸蔵、脱離しうる炭素材料を主体とする負極と集電体とを接合して一体化させたものを負極体という。正極体につ

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いても同様の定義とする。また、二次電池も電気二重層キャパシタも二次電源の1種であるが、本明細書では、正極に活性炭を含み、負極にリチウムイオンを吸蔵、脱離しうる炭素材料を含む特定の構成の二次電源を単に二次電源という。

【0010】本発明における電解液の溶媒としては、エチレンカーボネート、プロピレンカーボネート、ブチレンカーボネート、ジメチルカーボネート、エチルメチルカーボネート、ジエチルカーボネート、スルホラン、1, 2-ジメトキシエタン等が挙げられ、これらを単独で、又は2種以上の混合溶媒として使用できる。なかでも、正極の活性炭が電圧印加に対して安定である点で、プロピレンカーボネートを含む溶媒であることが好ましく、特にプロピレンカーボネートが70重量%以上含まれる溶媒であることが好ましい。

【0011】本発明における負極のリチウムイオンを吸蔵、脱離しうる炭素材料としては、黒鉛系炭素材料、低温焼成炭素材料、ハードカーボン等が挙げられるが、リチウムイオン吸蔵、脱離の電位が特に単な黒鉛系炭素材料が好ましい。ところが、プロピレンカーボネートを含む溶媒にリチウム塩を溶解した溶液中で、電気化学的方法で黒鉛系材料にリチウムイオンを吸蔵させようとしても、また前記溶液を電解液として充電してリチウムイオンを吸蔵させようとしても、リチウム参照極に対する電位が約0.8Vの付近でプロピレンカーボネートの電気分解が起こり、リチウムイオンを吸蔵できない。

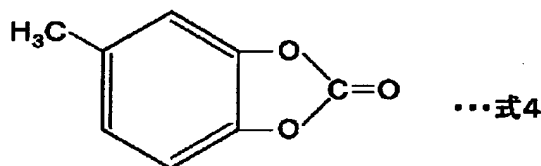
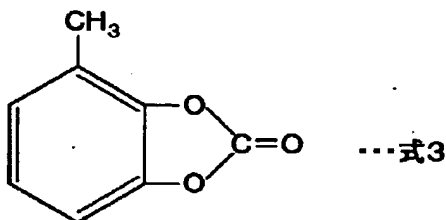
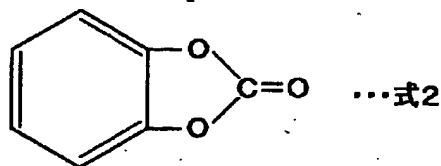
【0012】ところが、プロピレンカーボネートを含む溶媒にリチウム塩を溶解した溶液に式1で表される化合物(以下、化合物1と略記する)を添加すると、プロピレンカーボネートの分解が抑えられ、黒鉛系炭素材料にもリチウムイオンを吸蔵できる。

【0013】化合物1において、 R^1 及び R^2 は、それぞれ独立に水素原子又は炭素数1~10の直鎖状又は分岐状のアルキル基である。 R^1 及び R^2 の炭素数が多くなると、電解液に溶解しにくくなる。化合物1としては、具体的には式2で表されるカテコールカーボネート、式3で表される3-メチルカテコールカーボネート、式4で表される4-メチルカテコールカーボネート等が好ましい。

【0014】

【化3】

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【0015】化合物1を加えることによるプロピレンカーボネートの分解抑制のメカニズムの詳細は明らかではないが、プロピレンカーボネート溶液中の化合物1は、黒鉛系材料のリチウムイオン吸蔵時のプロピレンカーボネートの電気分解過程において、プロピレンカーボネート分子から生成した中間体ラジカルの捕捉剤として働き、黒鉛系材料表面にリチウムイオン導電性を有する表面皮膜を形成するものと思われる。その結果、さらなるプロピレンカーボネートの分解が防がれると思われる。

【0016】化合物1の電解液中の濃度は、0.1~15重量%であることが好ましい。0.1重量%未満では、この化合物を添加する効果が小さく、リチウムイオンを含むプロピレンカーボネート溶液中で黒鉛系材料にリチウムイオンを吸蔵できない。15重量%を超えると、二次電源の容量が小さくなり、充放電サイクルによる容量の低下が大きくなる。特に0.5~5重量%であることが好ましい。

【0017】リチウムイオン二次電池は、正極はリチウム含有遷移金属酸化物を主体とする電極、負極はリチウムイオンを吸蔵、脱離しうる炭素材料を主体とする電極であり、充電によりリチウムイオンが正極のリチウム含有遷移金属酸化物から脱離し、負極のリチウムイオンを吸蔵、脱離しうる炭素材料へ吸蔵され、放電により負極からリチウムイオンが脱離し、正極にリチウムイオンが吸蔵される。したがって、本質的には電解液中のリチウムイオンは電池の充放電に関与しない。

【0018】一方、本発明の二次電源は、充電により電解液中のアニオンが正極の活性炭に吸着し、電解液中の

リチウムイオンが負極のリチウムイオンを吸蔵、脱離しうる炭素材料へ吸蔵される。そして放電により負極からリチウムイオンが脱離し、正極ではアニオンが脱着する。すなわち、本発明の二次電源では充放電に電解液の溶質が本質的に関与しており、リチウムイオン電池とは充放電の機構が異なっている。そしてリチウムイオン二次電池のように、正極活物質自体にリチウムイオンが吸蔵、脱離することがなく、リチウムイオンの吸蔵、脱離にともなう正極の劣化がないため、本発明の二次電源は充放電サイクルによる劣化が少なく、長期的信頼性に優れている。

【0019】本発明では、負極の炭素材料には、あらかじめ化学的方法又は電気化学的方法によりリチウムイオンを吸蔵させることが好ましい。化学的方法としては、例えば負極炭素材料とリチウム金属を接触させた状態で電解液又はそれ以外のリチウム塩を溶解した有機溶媒中に浸漬し、リチウムをイオン化させて負極炭素材料に吸蔵させる方法がある。電気化学的方法としては、例えば負極炭素材料とリチウム金属をセパレータを介して対向させ、電解液中で定電流又は定電圧で前記負極炭素材料を充電する方法がある。

【0020】また、正極容量と負極容量がほぼ同等となるように形成すれば、負極の炭素材料に上記のようにあらかじめ化学的方法又は電気化学的方法によりリチウムイオンを吸蔵させなくても、二次電源の充電により負極の電位を十分に単にできる。すなわち、正極と負極の厚さが同程度であると負極容量が正極容量より大きいので二次電源の充電では負極の電位が十分に単にならないため、負極にあらかじめリチウムイオンを吸蔵しなくては高電圧の二次電源にならない。ところが、正極容量と負極容量がほぼ同じであれば、二次電源の充電だけで負極の電位を十分に単にできる。

【0021】具体的には、正極の厚さに対してセパレータを介して対向する負極の厚さが7~70%、さらには15~40%であることが好ましい。正極と負極の厚さの比がこの範囲であれば、正極の容量と負極の容量のバランスがとれ、高耐電圧の二次電源を構成できる。そして、正極の厚さは80~250 μ m、特に100~220 μ mであることが好ましい。80 μ m未満では二次電源の容量を大きくできない。また、250 μ mを超える場合は、充放電時に抵抗が上昇するため急速充放電するには実用的でない。

【0022】また、この場合、負極の厚さは、具体的には10~150 μ mが好ましい。10 μ m未満の厚さの負極は形成するのが難しい。特に好ましくは、正極の厚さが100~200 μ mかつ負極の厚さが20~50 μ mである。なお、本発明では正極及び負極は集電体の片面に形成しても両面に形成してもよいが、ここでいう正極及び負極の厚さとは、集電体の両面に形成される場合でも集電体の片面に形成されている電極層の厚さを示す

ものとする。

【0023】正極に含まれる活性炭は、比表面積が800~3000 m^2/g であることが好ましい。活性炭の原料、賦活条件は限定されないが、例えば原料としてはやしがら、フェノール樹脂、石油コークス等が挙げられ、賦活方法としては水蒸気賦活法、熔融アルカリ賦活法等が挙げられる。特にやしがら又はフェノール樹脂を原料として水蒸気賦活して得られる活性炭が好ましい。正極の抵抗を低くするために、正極中に導電材として導電性のカーボンブラック又は黒鉛を含ませるのも好ましく、このとき導電材は正極中に0.1~20重量%含まれることが好ましい。

【0024】正極体の作製方法としては、例えば活性炭粉末と導電材との混合物にバインダとしてポリテトラフルオロエチレンを混合し、混練した後シート状に成形して正極とし、これを集電体に導電性接着剤を用いて固定する方法がある。また、バインダとしてポリフッ化ビニリデン、ポリアミドイミド、ポリイミド等を溶解したワニスに活性炭粉末と導電材粉末とを分散させ、この液をドクターブレード法等によって集電体上に塗工し、乾燥して得てもよい。正極中に含まれるバインダの量は、正極体の強度と容量等の特性とのバランスから1~20重量%であることが好ましい。

【0025】本発明において、リチウムイオンを吸蔵、脱離しうる炭素材料はX線回折による〔002〕面の面間隔が0.335~0.410nmであることが好ましい。リチウムイオンを吸蔵、脱離しうる炭素材料には天然黒鉛、人造黒鉛、石油コークス、メソフェーズピッチ系炭素材料又は気相成長炭素繊維の熱処理温度を800~3000 $^{\circ}\text{C}$ の間で変えた材料、難黒鉛性炭素材料などがあるがいずれも使用できる。なかでも、特に抵抗が低い点から、〔002〕面の面間隔が0.335~0.338nmである黒鉛系炭素材料が好ましい。

【0026】上記黒鉛系炭素材料としては、具体的にはメソフェーズピッチ系炭素繊維、メソカーボンマイクロビーズ、気相成長炭素材料を2800 $^{\circ}\text{C}$ 以上で熱処理した炭素材料、及び天然黒鉛等が挙げられる。

【0027】本発明における負極体は、正極同様ポリテトラフルオロエチレンをバインダとして混練してシート状に成形して負極を形成し、導電性接着剤を用いて集電体に接着させて得ることができる。また、ポリフッ化ビニリデン、ポリアミドイミド又はポリイミドをバインダとし、バインダとなる樹脂又はその前駆体を有機溶媒に溶解させた溶液に前記炭素材料を分散させ、集電体に塗工し、乾燥させて得る方法もある。これらの方法はいずれも好ましい。

【0028】集電体に前記溶液を塗工して負極体を得る方法において、バインダとなる樹脂又はその前駆体を溶解させる溶媒は限定されないが、バインダを構成する樹脂又はその前駆体を容易に溶解でき、入手も容易である

ことからN-メチル-2-ピロリドン(以下、NMPという)が好ましい。ここで、ポリフッ化ビニリデンの前駆体、ポリアミドイミドの前駆体又はポリイミドの前駆体とは、加熱することにより重合してそれぞれポリフッ化ビニリデン、ポリアミドイミド又はポリイミドとなるものをいう。

【0029】上記のようにして得られるバインダは、加熱することにより硬化し、耐薬品性、機械的性質、寸法安定性に優れる。熱処理の温度は200℃以上であることが好ましい。200℃以上であれば、ポリアミドイミドの前駆体又はポリイミドの前駆体であっても通常重合して、それぞれポリアミドイミド又はポリイミドとなる。また、熱処理する雰囲気は窒素、アルゴン等の不活性雰囲気又は1 torr以下の減圧下が好ましい。ポリアミドイミド又はポリイミドは、本発明で使用する有機電解液に対する耐性があり、また負極から水分を除去するために300℃程度の高温加熱又は減圧下の加熱をしても充分耐性がある。

【0030】本発明において、負極と集電体の間にポリアミドイミド又はポリイミドからなる接着層を介在させると、負極と集電体の接着力はより強固になる。この場合、あらかじめ集電体にポリアミドイミド、ポリイミド又はこれらの前駆体を溶剤に溶解させたワニス、ドクターブレード法等の塗工法で塗工し、乾燥して接着層を形成し、この上に負極を形成する。また、接着層を形成するワニスに銅、黒鉛等の導電材を分散させておくと、負極と集電体との接触抵抗を低減できるので好ましい。この導電材を含むワニスは、活性炭を含む層をシート状に成形した場合における該層と集電体との間にも導電性接着剤として介在させることもできる。

【0031】本発明において、負極におけるリチウムイオンを吸蔵、脱離しうる炭素材料とバインダとの重量比は70:30~96:4が好ましい。バインダが30重量%より多いと、負極容量が小さくなる。バインダが4重量%未満であると、バインダとしての効果が弱くなり、負極と集電体との剥離が多くなる。

【0032】本発明における有機電解液に含まれるリチウム塩は、 LiPF_6 、 LiBF_4 、 LiClO_4 、 $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ 、 $\text{CF}_3\text{SO}_3\text{Li}$ 、 $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ 、 LiAsF_6 及び LiSbF_6 からなる群から選ばれる1種以上が好ましい。電解液中のリチウム塩の濃度は0.1~2.5 mol/L、さらには0.5~2 mol/Lが好ましい。

【0033】

【実施例】次に、実施例(例1~10)と比較例(例11~12)により本発明をさらに具体的に説明するが、本発明はこれらにより限定されない。なお、例1~12のセルの作製及び測定は、すべて露点が-60℃以下のアルゴングローブボックス中で行った。

【0034】[例1] フェノール樹脂を原料として水蒸

気賦活法によって得られた比表面積2000 m²/gの活性炭80重量%、導電性カーボンブラック10重量%、及びバインダとしてポリテトラフルオロエチレン10重量%からなる混合物をエタノールを加えて混練し、圧延した後、200℃で2時間真空乾燥して厚さ150 μmの電極シートを得た。この電極シートから4 cm×6 cmの電極を得て、ポリアミドイミドをバインダとする導電性接着剤を用いてアルミニウム箔に接合し、減圧下で300℃で10時間熱処理し、正極体とした。

10 【0035】次に、リチウムイオンを吸蔵、脱離しうる炭素材料として[002]面の面間隔が0.338 nmの黒鉛系炭素材料を用い、ポリアミドイミドをNMPに溶解した溶液に分散させて、銅からなる集電体に塗布して乾燥し、集電体上に負極を形成した。負極中のリチウムイオンを吸蔵、脱離しうる炭素材料とポリアミドイミドとは重量比で9:1であった。これをさらにロールプレス機でプレスし、負極の面積を6 cm×4 cm、厚さを15 μmとし、減圧下で260℃で10時間熱処理し、負極体とした。

20 【0036】上記正極体と上記負極体とを、ポリプロピレン製セパレータを介してそれぞれの電極面を対向させ、挟持板で挟持して素子を作製した。プロピレンカーボネートにカテコールカーボネート(式2)を2重量%、及び LiBF_4 を1 mol/Lの濃度で溶解した溶液を電解液とし、前記素子を充分に含浸させて、4.2 Vから3 Vまでの範囲で初期容量を測定した。その後、充放電電流10 mA/cm²で、4.2 Vから3 Vまでの範囲で充放電サイクルを行い、2000サイクル後の容量を測定し、容量の変化率を算出した。結果を表1に示す。

30 【0037】[例2] カテコールカーボネート(式2)のかわりに3-メチルカテコールカーボネート(式3)を用いた以外は例1と同様にして二次電源を得て、例1と同様に評価した。結果を表1に示す。

【0038】[例3] カテコールカーボネート(式2)のかわりに4-メチルカテコールカーボネート(式4)を用いた以外は例1と同様にして二次電源を得て、例1と同様に評価した。結果を表1に示す。

40 【0039】[例4] カテコールカーボネート(式2)の量を0.05重量%に変更した以外は例1と同様にして二次電源を得て、例1と同様に評価した。結果を表1に示す。

【0040】[例5] カテコールカーボネート(式2)の量を20重量%に変更した以外は例1と同様にして二次電源を得て、例1と同様に評価した。結果を表1に示す。

50 【0041】[例6] フェノール樹脂のかわりに、やしがらを原料として水蒸気賦活法によって得られた比表面積2000 m²/gの活性炭を用いた以外は例1と同様にして、電極面4 cm×6 cm、厚さ150 μmの正極

が集電体に接合された正極体を得た。

【0042】次に、リチウムイオンを吸蔵、脱離しうる炭素材料として、[002]面の面間隔が0.337nmの黒鉛系炭素材料を用いた以外は例1と同様にして、電極面4cm×6cm、厚さ200μmの負極が集電体に接合された負極体を得た。この負極を作用極とし、ニッケルメッシュにリチウム金属を固定したものを対極及び参照極として、例1と同じ電解液中で負極に電気化学的方法により290mAh/gとなるまでリチウムイオンを吸蔵させた。上記正極体と上記負極体とを用いた以

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外は例1と同様にして二次電源を得て、例1と同様に評価した。結果を表1に示す。

【0043】[例7]カテコールカーボネート(式2)のかわりに3-メチルカテコールカーボネート(式3)を用いた以外は例6と同様にして二次電源を得て、例6と同様に評価した。結果を表1に示す。

【0044】[例8]カテコールカーボネート(式2)のかわりに4-メチルカテコールカーボネート(式4)を用いた以外は例6と同様にして二次電源を得て、例6と同様に評価した。結果を表1に示す。

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【0045】[例9]カテコールカーボネート(式2)の量を0.05重量%に変更した以外は例6と同様にして二次電源を得て、例6と同様に評価した。結果を表1に示す。

【0046】[例10]カテコールカーボネート(式2)の量を20重量%に変更した以外は例1と同様にして二次電源を得て、例6と同様に評価した。結果を表1に示す。

【0047】[例11]電解液として、カテコールカーボネート(式2)を添加しない1mol/LのLiBF₄を含むプロピレンカーボネート溶液を用いた以外は例

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1と同様にして二次電源を得て、例1と同様に評価した。結果を表1に示す。

【0048】[例12]電解液として、カテコールカーボネート(式2)を添加しない1mol/LのLiBF₄を含むプロピレンカーボネート溶液を用いた以外は例6と同様にして二次電源を得て、例1と同様に評価した。結果を表1に示す。

【0049】

【表1】

	初期容量 (mAh)	容量変化率 (%)
例1	1.95	-6.8
例2	1.92	-7.3
例3	1.94	-6.9
例4	1.67	-11.7
例5	1.62	-12.9
例6	2.43	-5.4
例7	2.41	-5.7
例8	2.31	-5.8
例9	2.30	-9.6
例10	2.28	-10.4
例11	0.19	-71.6
例12	0.21	-68.9

【0050】

【発明の効果】本発明によれば、充放電サイクルにおいて正極に対しても負極に対しても安定な電解液を使用できるため、耐電圧が高く、容量が大きくかつ急速充放電サイクル信頼性の高い二次電源を提供できる。

フロントページの続き

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